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(54) Gemini tensides, tenside mixture and cleaning agent

(57) The invention concerns a Gemini tenside of the general formula I

/formula/

(I)

as well as its use in laundry detergents, cleaning agents for hard surfaces, body cleansing agents, cosmetics, dish washer detergents, dish detergents, as industrial emulsifiers, wetting agents, dispersing agents, particularly in lacquers and paints, demulsifiers, hydrotropic agents, antistatic agents, additives for the oil industry, fuel additives or for uses in the metal and textile processing industry.

Another object of the invention consists of a tenside mixture that contains

- a) between 0.1% by weight and 99% by weight of at least one tenside with at least two hydrophilic and at least two hydrophobic groups, in which case the hydrophilic groups and the hydrophobic groups are separated by a linear or cyclic spacer (Gemini tenside) that contains at least four C-atoms, as component A, and
- b) between 0 and 99% by weight of at least one non-ionic tenside that is not a Gemini tenside as component B and/or
- c) between 0 and 99% by weight of at least one anionic tenside that is not a Gemini tenside as component C,

in which case the sum of the percentage contents of components A, B and C must be 100%.

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European Patent Office

EUROPEAN SEARCH REPORT

Application No. EP 98 10 9998

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This searc	h report was prepared	for all patent claims.		
1	ch conducted in	Completion dat	e	By
THE HAC		January 14, 2000	Ric	hards, M
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X: Of par	ticular significance wh	nen considered P: In	ntermediate li	terature.
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			pplication dat	

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APPENDIX FOR THE EUROPEAN SEARCH REPORT ON THE EUROPEAN PATENT APPLICATION NO.

EP 98 10 9998

This appendix indicates the members of the patent family of the patent documents listed in the above-mentioned European Search Report.

Information on the family members corresponds to the current data maintained by the European Patent Office.

These data are provided as information only and are not guaranteed.

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See Official Gazette No. 12/82 of the European Patent Office regarding further details for this appendix.

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(54) Gemini tensides, tenside mixture and cleaning agent

(57) The invention concerns Gemini tensides and tenside mixtures that contain them, their use in cleaning agents, particularly in HGSM, and cleaning agents, particularly HGSM, that contain such Gemini tensides and tenside mixtures.

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Description

The invention concerns Gemini tensides and tenside mixtures that contain so-called "Gemini tensides". Furthermore, the invention concerns the use of tenside mixtures that contain Gemini tensides in cleaning agents - particularly in HGSM - and cleaning agents - particularly HGSM - that contain Gemini tensides.

Within the scope of this text, the term "Gemini tensides" refers to compounds that contain at least two hydrophilic groups and at least two hydrophobic groups per molecule.

Gemini tensides are known, for example, from M. Rosen, Chemtec (1993), page 20 and following; F. Menger, C.A. Litau, J.Am.Chem.Soc. 115 (1993), page 1083 and following. The tensides described in the referenced literature are characterized by an unusually low critical micelle concentration and the ability to strongly reduce the surface tension of the water.

Cleaning agents such as laundry detergents and particularly HGSM often exhibit the disadvantage that no satisfactory flushing or cleaning effect can be achieved when the supply is too low or the temperature of the flushing or cleaning liquid is too low. This can often be traced to the fact that the tensides contained in the cleaning agent and particularly in the HGSM no longer have a sufficient cleaning power under the application conditions.

Document WO-A 96/23768 describes the manufacture of Gemini tensides from dimer and trimer alcohols. A combination with the thus obtainable Gemini tensides with other tensides in cleaning agents or HGSM is not mentioned there.

The known Gemini tensides are often expensive and costly to produce. Document WO-A 96/16033 concerns Gemini tensides prepared from epoxies and polyols. Not disclosed are Gemini tensides, whose á-C-atom of the originally used epoxy forms a CH₂-group after reacting with a polyol and that are subsequently alkoxylated with at least one mol alkoxide per remaining OH-group and are then sulfated. Furthermore, nothing is said about their superb cleaning power.

Accordingly, the task of the invention consists in the presentation of a Gemini tenside class that is easy to prepare and exhibits an excellent cleaning power by itself or preferably in a mixture with other tensides.

A further task of the invention consists in the presentation of a tenside mixture that shows an improved cleaning power in cleaning agents and particularly in HGSM.

It was found that compounds of the general formula I

/formula/ (I)

- where R^1 and R^2 represent hydrogen and/or C_{1-6} -alkyl independently of each other, R^3 , R^4 , R^5 and R^6 represent hydrogen or linear or branched alkyl rests with 4 to 24 C-atoms independently of each

other, n represents numbers between 2 and 10, m and p represent numbers of 1 to 40 independently of each other, X and Y represent hydrogen, CH₂-COOM or SO₃M stet independently of each other and M represents hydrogen or alkali or earth alkali metal ion, in which case one of the two rests of the rest pairs R³ and R⁴ as well as R⁵ and R⁶ must represent hydrogen - are easy to prepare and exhibit an excellent cleaning power in cleaning agents.

Accordingly, the object of the invention consists in a compound of the general formula I, where R¹ and R² represent hydrogen independently of each other and/or C₁₋₆-alkyl, R³, R⁴, R⁵ and R⁶ represent hydrogen or linear or branched alkyl rests with 4 to 24 C-atoms independently of each other, n represents numbers of between 2 and 10, m and p represent numbers of between 1 and 40 independently of each other, X and Y represent hydrogen, CH₂-COOM or SO₃M independently of each other and M represents hydrogen or alkali or earth alkali metal ion, in which case one of the two rests of the rest pairs R³ and R⁴ as well as R⁵ and R⁶ must represent hydrogen.

Within the scope of this invention, the term "hydrogen and/or C₁₋₆ alkyl" indicates that the general formula I also includes compounds that carry mixed polyether chains. Mixed polyether chains can be produced with an alkoxylation with at least two different alkoxides such as ethylene oxide (EO) and propylene oxide (PO), i.e., either in blocks or mixed. Thus are obtained either polyether chains with defined successive blocks of alkoxides EO-EO-PO-PO-PO-EO-EO-EO ...)or statistically mixed chains (e.g. EO-EO-PO-PO-PO-PO-EO-PO-EO-EO...). Within the scope of this invention, formula I includes compounds with polyether chains that contain just one alkylene oxide type as well as compounds with polyether chains that contain two or more different alkylene oxides and can be arranged successively in blocks or statistically.

It is particularly preferred, when R¹ and R² represent hydrogen and/or CH₃ independently of each other. It is also preferred, when R³ and R⁴ represent an unbranched alkyl rest with more than 10 carbon atoms, in which case the respective remaining rest represents hydrogen. It is also preferred, when R⁵ or R⁶ represent an unbranched alkyl rest with more than 10 carbon atoms, in which case the respective remaining rest represents hydrogen. It is particularly preferred, when R³ and R⁴ represent an unbranched alkyl rest with between approximately 12 and 16 carbon atoms, in which case the respective remaining rest represents hydrogen. It is also preferred, when R⁵ or R⁶ represent an unbranched alkyl rest with between approximately 12 and 16 carbon atoms, in which case the respective remaining rest represents hydrogen.

It is also preferred, when n represents the numbers 2 through 8 such as 2, 3, 4, 5, 6 or 7. Furthermore, it is preferred when m and p represent independently of each other numbers of between 3 and approximately 30 and preferably of between approximately 8 and 20. In that regard, the expert immediately recognizes that the nature of the alkoxylation reaction points to an average number. Individual molecules may deviate from this average number due to the homologous distribution that forms. Accordingly, the number does not need to be a natural number; fractions such as 8.5, 9.3, 10.7, 11.4 may occur. Generally (and assuming a complete reaction), the average number may be equal to the established molar ratio between alkoxide and OH-groups. In a particularly preferred manner, m and p represent independently of each other numbers between approximately 8 and 12 and particularly preferred represent approximately the number 10.

X and Y preferably represent SO_3M , in which case M represents hydrogen or alkali or earth alkali metal ion, particularly sodium, or quaternized stock material bases such as ammonium ions or quaternized amines for C_{1-18} -alkyl rests that possibly carry functional groups (e.g., hydroxyl groups).

The compounds of the general formula I are excellent in cleaning agents such as in laundry detergents, cleaning agents for hard surfaces, body cleaning agents, cosmetics, dish washer detergents, dish detergents, as industrial emulsifiers, wetting agents, dispersing agents, particularly in lacquers and pints, demulsifiers, hydrotropic agents, antistatic agents, additives for the oil industry, fuel additives or for uses in the metal and textile process industry.

Accordingly, the object of the invention also consists in the use of compounds of the general formula I in laundry detergents, cleaning agents for hard surfaces, body cleaning agents, cosmetics, dish washer detergents, dish detergents, as industrial emulsifiers, wetting agents, dispersing agents, particularly in lacquers and paints, demulsifiers, hydrotropic agents, antistatic agents, additives for the oil industry, fuel additives or for uses in the metal and textile process industry.

The compounds designated with the general formula I belong to the class of Gemini tensides that will be explained in more detail at a later point in the text.

Furthermore, it was found that Gemini tensides exhibit an improved cleaning power when mixed with at least one non-ionic tenside and at least an anionic tenside, i.e., in comparison with cleaning agents generally used until now and particularly with HGSM.

Accordingly, a further object of the invention consists of a tenside mixture that contains

a) between 0.1% by weight and 99% by weight of at least one tenside with at least two hydrophilic and at least two hydrophobic groups, in which case the hydrophilic groups and the hydrophobic groups are separated from each other by a linear or cyclic spacer, containing at least four C-atoms (Gemini tenside) as component A

and

b) between 0 and 99% by weight of at least one non-ionic tenside that is not a Gemini tenside as component B

and/or

c) between 0 and 99% by weight of at least one anionic tenside that is not a Gemini tenside as component C, in which case the sum of the percentage contents of components A, B and C must be 100%.

Within the scope of this invention, the term "cleaning agent" refers to an agent that is initially available to the user in a concentrated form and is dissolved for its use in water at a temperature up to approximately 60 °C. With this cleaning liquid, it is possible to then clean

textiles, hard surfaces such as glass, ceramics, concrete, metal as well as lacquered or polished surfaces.

The HGSM represent a sub-group of cleaning agents. For their use, HGSM are generally dissolved in water at a temperature of or up to approximately 50 °C and the thus prepared cleaning liquid is used to clean eating and cooking utensils.

While the Gemini tensides described in the above-mentioned references are difficult to produce synthetically, WO-A 96/23768 describes a simple method for the production of Gemini tensides from dimer and/or trimer alcohols.

Dimer and trimer alcohols are commercially available compounds and may be obtained by reducing dimer- and/or trimer fatty acid esters that themselves are obtained, for example, with the oligomerization of unsaturated fatty acids and a subsequent esterification. The thus obtained dimer and trimer fatty acids generally consist of mixtures of acyclic and cyclic dicarbonic acids with an average of between 36 and 44 carbon atoms (see A. Hinze, Fats & Oils, 26, (1994).

Dimer- and/or trimer alcohol alkoxylates may be produced in a generally known manner through an alkoxylation of the dimer and/or trimer alcohols. To the group of alkoxylates preferably used to produce Gemini tensides belong, for example, the ethoxylates and propylates or mixed alkoxylates that contain ethoxy as well as propoxy groups. Particularly preferred are addition compounds with an average of between 1 and 20 ethylene oxide groups per substituted OH group, in which case between 1 and approximately 5 propylene oxide groups per substituted OH group may be present additionally. The alkoxylation degrees indicated represent statistical average numbers that can be a full or fractional number for a special product. Preferred dimer- or trimer alcohol alkoxylates exhibit a narrow homologous distribution with respect to the number of alkylene oxide units (narrow range ethoxylates, NRE).

The alkoxylated dimer- and/or trimer alcohol alkoxylates are sulfated with generally known sulfation agents such as sulfuric acid, oleum, chlorosulfonic acid, aminosulfonic acid and/or gaseous sulfur trioxide, possibly mixed with an inert gas, sulfated, in which case chlorosulfonic acid and gaseous sulfur trioxide are preferred.

After the sulfation reaction, the prepared products are neutralized with a base and are preferably set to a pH-value of less than 9 and particularly preferred to between approximately 6.5 and 8.5. Bases for the neutralization may consist of alkali metal hydroxides such as lithium-, sodium or potassium hydroxide, earth alkali metal oxide and earth alkali metal hydroxides such as magnesium oxide, calcium oxide or calcium hydroxide, ammonia, mono-, di- or tri-alcohol amines with between 2 and 4 carbon atoms, as well as primary, secondary or tertiary C₁₋₄-alkyl amines, or mixtures of 2 or more thereof.

A distinct reference is hereby made again to the content of WO-A 96/23768 regarding the sulfation and neutralization reaction.

The thus obtainable dimer- and/or trimer alcohol-bis- or tris-ether-sulfates used within the scope of the presented invention have boundary surface-active properties. They do promote, for

example, the wetting of solid surfaces and the emulsifying phases that could not be mixed otherwise.

Accordingly and in a preferred design form of the invention, component A consists of at least one dimer alcohol-bis-ether sulfate or of at least one trimer alcohol-tris-ether sulfate that can be produced by reacting the addition reaction products of dimer- and/or trimer alcohols or mixtures of such addition reaction products with a sulfation agent and by a subsequent neutralizing with an aqueous base.

Component A may also consist of the earlier described compounds with the general formula I that may be obtained with the ring-opening reaction of at least 2 mol epoxidized á-olefin with between approximately 6 and 26 C-atoms and 1 mol alkylene diol such as ethylene glycol, propylene glycol, butane diol-1,4, pentane diol-1,5, hexane diol-1,6, heptane diol-1,7 or octane diol-1,8 with a subsequent alkoxylation and preferably ethoxylation of the produced OH-groups, and with a subsequent sulfation.

Accordingly and in another preferred design form of the invention, component A consists of at least one compound of the general formula I, where R¹ and R² represent hydrogen and/or C₁₋₆-alkyl independently of each other, R³, R⁴, R⁵ and R⁶ represent hydrogen or linear or branched alkyl rests with 4 to 24 C-atoms independently of each other, m and p represent numbers of between 1 and 40 independently of each other, X and Y represent hydrogen, CH₂-COOM or SO₃M independently of each other and M represents hydrogen or alkali or earth alkali metal ion, in which case one of the two rests of the rest pairs R³ and R⁴ as well as R⁵ and R⁶ must represent hydrogen.

It is particularly preferred that R¹ and R² represent hydrogen and/or CH₃ independently of each other. It is also preferred that R³ or R⁴ represent an unbranched alkyl rest with more than 10 carbon atoms, in which case the remaining rest represents hydrogen. It is also preferred that R⁵ and R⁶ represent an unbranched alkyl rest with more than 10 carbon atoms, in which case the remaining rest represents hydrogen. It is particularly preferred that R³ and R⁴ represent an unbranched alkyl rest with between approximately 12 and 16 carbon atoms, in which case the remaining rest represents hydrogen. Accordingly, it is also preferred that R⁵ or R⁶ represent an unbranched alkyl rest with between approximately 12 and 16 carbon atoms, in which case the remaining rest represents hydrogen.

It is also preferred that n represents a number of between 2 and 8 such as 2, 3, 4, 5, 6 or 7. Furthermore, it is preferred that m and p represent - independently of each other - numbers of between 3 and 30 and preferably of between approximately 8 and 20. In that regard, the expert immediately recognizes that the nature of the alkoxylation reaction points to an average number. Individual molecules may deviate from this average number due to the homologous distribution that forms. Accordingly, the number does not need to be a natural number; fractions such as 8.5, 9.3, 10.7, 11.4 may occur. Generally (and assuming a complete reaction), the average number may be equal to the established molar ratio between alkoxide and OH-groups. In a particularly preferred manner, m and p represent independently of each other numbers between approximately 8 and 12 and particularly preferred represent approximately the number 10.

X and Y preferably represent SO₃M, in which case M represents hydrogen or alkali or earth

alkali metal ion, particularly sodium.

Component A of the tenside mixture in accordance with the invention may contain just one Gemini tenside; however, it is also possible to use mixtures of two or more Gemini tensides as component A.

In any case, the percentage content of component A in the tenside mixture in accordance with the invention varies between approximately 0.1 and 99% by weight and preferably between approximately 1 and 98% by weight. It is preferred that the percentage content of component A in the tenside mixture in accordance with the invention varies between approximately 10% by weight and 60% by weight and preferably between approximately 15% by weight and 55% by weight and particularly preferred between approximately 20% by weight and 50% by weight.

The tenside mixture in accordance with the invention contains at least one non-ionic tenside that is not a Gemini tenside as component B.

Typical examples of non-ionic tensides consist of fatty alcohol alkyl ethers, preferably with ethylene oxide or propylene oxide units, alkyl phenol polyalkylene ethers, preferably with ethylene oxide or propylene oxide units, fatty acid polyalkylene esters, preferably with ethylene oxide or propylene oxide units, fatty acid amide polyalkylene ethers, preferably with ethylene oxide or propylene oxide units, fatty amine polyalkylene ether, preferably with ethylens oxide or propylene oxide units, alkoxylated triglycerides, preferably alkoxylated with ethylene oxide or propylene oxide, amine oxides, alk(en)yl oligoglucosides, fatty acid-N-alkyl glucamides, protein hydrolysates, (particularly plant products on a soja base), polyol fatty acid esters, sugar esters, sorbitan esters and polysorbates. When the non-ionic tensides contain polyalkylene ether chains, they may have a conventional and preferably a narrow homologous distribution.

For example: As component B in the effective substance, the cleaning agents used by hand and particularly HGSM in accordance with the invention contain at least one addition reaction product of alkylene oxide on linear aliphatic C_{8-16} -alcohol. Ethylene oxide and/or propylene oxide are preferred alkylene oxides. Particular preference is given to ethylene oxide; however, it is also possible to use compounds with mixed ether chains that contain ethylene oxide as well as propylene oxide, i.e., in a random order or as sequential blocks.

Typical examples of fatty alcohols are caproin alcohol, capryl alcohol 2-ethyl hexyl alcohol, caprin alcohol, lauryl alcohol, isotridecyl alcohol, myristyl alcohol, cetyl alcohol, palmoleyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, elaidyl alcohol, petroselinyl alcohol, behenyl alcohol erucyl alcohol and brassidyl alcohol as well as their industrial mixtures that are obtained, for example, during the high-pressure hydration of industrial methyl esters on the basis of fats and oils or aldehydes from the Roelen oxosynthesis as well as a monomer fraction during the dimerization of unsaturated fatty alcohols. Preference is given to industrial fatty alcohol mixtures, in which case the obtained fatty alcohols contain between approximately 12 and 18 carbon atoms such as cocinic, palm, palm pit or tallow fat alcohols and particularly the ethoxylation product of cocinic fatty alcohols, in which case the alcohol contains approximately 7 ethylene oxide units on average.

Also usable as component B are amides of alkyl carbonic acid and preferably of alkyl carbonic acid with between approximately 6 and 24 C-atoms, with alkanol amides and preferably monoalkanol amides. From this group, particular preference is given to the amines that can be produced from naturally or synthetically prepared fatty acids and fatty acid sections with aminoethanol and particularly preferred are monoethanol amides from cocinic fatty acid sections, particularly the C_{8-14} -fatty acid sections and ethanol amine.

In a preferred manner, at least one alkyl polyglycoside or at least one fatty acid glucamide is used as component B. In the cleaning agent in accordance with the invention and particularly in the HGSM, the respective non-ionic tenside can serve as a wetting agent or can be used to better dissolve fat-containing substances.

An alkyl polyglycoside of the general formula II is particularly preferred as component B:

/formula/ (II),

where R^3 represents a linear or branched $C_{6\text{-}22}$ -alkyl rest, Z represents any mono- or oligo saccharide and x represents a number of between 1 and 5. In a preferred manner, R_3 represents alkyl rests that are linear or methyl-branched in position number 2. Such alkyl rests consist, for example, of 1-octyl, 1-decyl-, 1-lauryl-, 1-myristyl-, 1-cetyl- and 1-stearyl rests. Particularly preferred are 1-octyl-, 1-decyl-, 1-lauryl- or 1-myristyl rests. Alkyl rests R_3 with an odd number of carbon atoms in the alkyl chain dominated with the use of so-called "oxo-alcohols" as initial materials for the production of compounds of the general formula II.

The alkyl polyglycosides that can be used as component B may contain just one specific alkyl rest R₃. However, the alkyl polyglycosides are generally produced on the basis of natural fats and oils or mineral oils. In this case, the alkyl rests R₃ mixtures are present according to the initial compounds or according to the respective processing of these compounds.

Particular preference is given to those alkyl polyglycosides, in which R³ basically represents

- C_8 and C_{10} -alkyl groups,
- C₁₂- and C₁₄-alkyl groups,
- C₈- to C₁₆-alkyl groups,
- C_{12} to C_{16} -alkyl groups.

The sugar building block Z is derived from any mono- or oligo saccharides. Sugar with 5 or 6 carbon atoms as well as the respective oligosaccharides are generally used. Such sugars may consist of glucose, fructose, galactose, arabinose, ribose, xylose, lyxose, allose, altrose, mannose, gulose, idose, talose and sucrose. Preferred sugar building blocks are glucose, fructose, galactose, arabinose and sucrose. Particular preference is given to glucose.

Per alkyl glycoside unit, the alkyl polyglycosides that can be used in accordance with the invention contain between approximately 1.1 and 5 sugar units on average. Preferred are alkyl polyglycosides with numbers x of between approximately 1.2 and 1.8. Particularly preferred are

alkyl polyglycosides, for which x varies between approximately 1.3 and 1.6.

The alkoxylated homologues substance of the above-mentioned alkyl polyglycosides can be used already in accordance with the invention. On average, these homologues may contain up to 10 ethylene oxide and/or propylene oxide units per alkyl glycoside unit.

Tensides from the family of the glucamides such as alkyl-N-methyl glucamide, in which the term "alkyl" refers to the alkyl rest with a chain length of between approximately 6 and 14 carbon atoms, can also be utilized for the hand-used cleaning agents in accordance with the invention and particularly for HGSM. It may be advantageous when the described non-ionic tensides do not form the sole component of component B, but are used in a mixture with at least another non-ionic tenside, e.g., in combination with fatty alcohol ethoxylate and/or glucamide. It is also possible to use quaternary or even higher combinations of the non-ionic tensides disclosed here.

Component B is contained in the tenside mixture in accordance with the invention possibly at a percentage content of up to 99% by weight and preferably at a percentage content of between approximately 10% by weight and 80% by weight. Particularly preferred are contents of between approximately 15% by weight and 55% by weight, for example between approximately 20 and 40% by weight.

The ratio between component A and component B in the cleaning agent in accordance with the invention, particularly in HGSM, generally varies between approximately 1:4 and 4:1 and preferably between approximately 1:2 and 2:1.

As component C, the tenside mixture in accordance with the invention possibly contains at least one anionic tenside that is not a Gemini tenside.

Typical examples of anionic tensides that can be used within the scope of the invention consist of alkyl benzene sulfonates, alkane sulfonates, olefin sulfonates, alkyl ether sulfonates, glycerin ether sulfonates, sulfo fatty acids, alkyl sulfates, fatty alcohol ether sulfates, glycerine ether sulfates, hydroxy mixture ether sulfate, monoglyceride (ether) sulfate, fatty acid amide (ether) sulfate, dialkyl succinate, mono- and dialkyl sulfosuccinamates sulfotriglycerides, amide soaps, ether carbonic acid and their salts, fatty acid isothionates, fatty acid sarcosinates, fatty acid taurides, acyl acetates, acyl oligoglycoside sulfates, protein fatty acid condensates (particularly plant products on a soya basis) or alkyl (ether) phosphate or mixtures of two or more thereof.

In a preferred manner, component C of the tenside mixture in accordance with the invention contains at least one anionic tenside selected from the group of alkyl sulfates, alkyl ether sulfates, alkane sulfonates, alkyl benzenol sulfonates or olefin sulfonates.

Within the scope of the invention, anionic tensides from the alkyl sulfates are particularly preferred as component C or a part of component C. This may include tensides of the general formula III

/formula/ (III)

where R^4 represents an aliphatic, linear and/or branched C_{6-22} -alkyl rest and M represents a metal cation or ammonium ion.

Anionic tensides that can be used within the scope of the invention may also consist of fatty alcohol ether sulfates that are produced on a large scale with an SO₃ or chlorosulfonic acid (CSA) sulfation of fatty alcohol polyalkylene ethers and a subsequent neutralization. Typical examples consist of sulfates from addition reaction products of 1-10 and particularly of 2-5 mol ethylene oxide on average of caproin alcohol, caproyl alcohol, 2-ethyl hexyl alcohol, caprin alcohol, lauryl alcohol, isotridecyl alcohol, myristyl alcohol, palmoleyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, elaidyl alcohol, petroselinyl alcohol, arachyl alcohol, gadoleyl alcohol, behenyl alcohol, erucyl alcohol and brassidyl alcohol as well as their industrial mixtures, in which case the sulfates are generally used as alkali salt, preferably as sodium salt or as earth alkali metal salt, preferably as magnesium salt, or as a mixture of two or more of the last-mentioned salts.

The tenside mixture in accordance with the invention contains component C with a percentage content of up to approximately 99% by weight and preferably up to approximately 80% by weight. Particularly preferred is a component C content of between approximately 5% by weight and 70% by weight, in which case a content of between approximately 20% by weight and 60% by weight is preferred.

Accordingly, the tenside mixture in accordance with the invention preferably contains

- between approximately 0.1 and 99% by weight component A,
- between approximately 0 and 99% by weight component B and
- between approximately 0 and 99% by weight component C,

in which case the sum of the percentage contents of components A, B and C must be 100%.

The tenside mixture in accordance with the invention must contain at least a combination of components A and B or of A and C. In the first case, a preferred tenside mixture contains between approximately 20% by weight and 45% by weight of component A and between approximately 80 and 55% by weight of component B. In the latter case, the tenside mixture contains between approximately 10% by weight and 35% by weight of component A and between approximately 15% by weight and 50% by weight of component C.

In a preferred design form, however, the tenside mixture in accordance with the invention contains all three components A, B and C. In this case, tenside mixtures with the following composition are preferred:

Component A: between approximately 20% by weight and 50% by weight, Component B: between approximately 15% by weight and 35% by weight, Component C: between approximately 20% by weight and 60% by weight,

or

Component A: between approximately 15% by weight and 35% by weight,

Component B: between approximately 30% by weight and 70% by weight, Component C: between approximately 1% by weight and 45% by weight.

In a preferred design form of the invention, the combination of components A, B and C must be 100%.

The described tenside mixtures can be used in cleaning agents and particularly in HGSM. Accordingly, the object of the invention also consists of a cleaning agent and particularly a HGSM containing a tenside mixture that contains

a) between 0.1% by weight and 99% by weight of at least one tenside with at least two hydrophilic and at least two hydrophobic groups, in which case the hydrophilic groups and the hydrophobic groups are separated by a linear or cyclic spacer (Gemini tenside) that contains at least four C-atoms, as component A,

and

b) between 0 and 99% by weight of at least one non-ionic tenside that is not a Gemini tenside as component B

and/or

c) between 0 and 99% by weight of at least one anionic tenside that is not a Gemini tenside as component C, in which case the sum of the percentage contents of components A, B and C must be 100%. In addition to components A, B and C, the agent in accordance with the invention may also contain other additives such as solvents, builders, abrasive substances, dyes and/or aromatics.

The solvent for the agent in accordance with the invention may consist of water or low mono- or polyalcohols such as ethanol, isopropanol, ethylene glycol, propylene glycol, alkanol amine or glycerin. In relation to the whole agent, the solvents may be present at a quantity of up to 50% by weight in the agent in accordance with the invention; a lower quantity is preferred, however.

Within the scope of this invention, the term "builders" refers to compounds that take on central tasks in the cleaning process. They not only contribute to the washing phase through special effects, but also affect the power of the other cleaning agent components in a decisive manner, e.g., of tensides or bleaching agents. The effects offered by the builders may include the elimination of the so-called "hardness formers" from the cleaning liquid and material to be cleaned as well as the dispersing of dissolved dirt and other suspended substances.

Possibly suitable builders consist of those from the class of aminopolycarbonic acids and polyphosphonic acids. Aminopolycarbonic acids include nitrilo triacetic acid, diethylene triamine penta-acetic acid as well as the higher homologues. Suitable polyphosphonic acids are 1-hydroxyethane-1,1-diphosphonic acid, amino-tri(methylene phosphonic acid), ethylene diamine tetra- (methylene phosphonic acid) and their higher homologues such as diethylene tetra-amine

tetra(methylene phosphonic acid). These acids are generally used in the form of their alkali salts, particularly the sodium or potassium salts. Preference is given to sodium nitrilo triacetate in a percentage content of up to 10% by weight and preferably of between 2% by weight and 6% by weight in relation to the cleaning agent or particularly to HGSM.

Other suitable builders consist of monomeric polycarbonic acids or hydroxy polycarbonic acids and particularly in the form of alkali salts such as sodium citrate and/or sodium gluconate.

Preferably used builders include homopolymeric and/or copolymeric carbonic acids or their alkali salts, in which case the sodium or potassium salts are preferred. Particularly suited are polymeric carboxylates or polymeric carbonic acids - with a relative molecular weight M_n of at least 350 - in the form of their water-soluble salts and particularly in the form of the sodium and/or potassium salts such as oxidized polysaccharides according to WO-A 93/08251, polyacrylate, polyhydroxy acrylate, polymethacrylate, polymaleate and particularly copolymers of the acrylic acid with maleic acid or maleic acid anhydride, preferably those consisting of between 50 and 70% by weight acrylic acid and between 50 and 10% by weight maleic acid as characterized in EP-A 0 022 551. The relative molecular weight M_n of the homopolymers generally varies between 1,000 and 100,000 and that of the copolymers between 2,000 and 200,000 and preferably between 50,000 and 120,000 in relation to the free acid.

Particularly preferred acrylic acid/maleic acid copolymers have a relative molecular weight M_n of between 50,000 and 100,000.

Suitable - though less preferred- compounds of this class consist of copolymers of the acrylic acid and/or methacrylic acid with vinyl ethers such as vinyl methyl ethers, vinyl esters, ethylene, propylene and/or styrene, in which the percentage content of the respective acid or the percentage content of mixture of acids is at least 50% by weight.

The polymeric carboxylate or carbonic acids may also consist of terpolymers, whose monomers consist of two carbonic acids and/or their salts and whose third monomer consists of vinyl alcohol and/or vinyl alcohol derivatives or of a carbon hydrate. The first acid monomer or its salt is obtained from a mono-ethylenically unsaturated C₃₋₈-carbonic acid and preferably from a C₃₋₄-monocarbonic acid, particularly from the (meth)acrylic acid. The second acid monomer or its salt may consist of a derivative of a C₄₋₈-dicarbonic acid and preferably of a C₄₋₈-dicarbonic acid, in which case maleic acid is preferred. In this case, the third monomeric unit is formed by vinyl alcohol and/or preferably an esterified vinyl alcohol. Particularly preferred are vinyl alcohol derivatives that represent an ester from short-chained carbonic acids such as C₁₋₄-carbonic acids with vinyl alcohol. In that regard, preferred terpolymers contain between 60 and 95% by weight and particularly between 70 and 90% by weight (meth)acrylic acid or (meth)acrylate and particularly preferred acrylic acid or acrylate and maleic acid or maleate as well as between 5 and 40% by weight and preferably between 10 and 30% by weight vinyl alcohol and/or vinyl acetate. In that regard, much preference is given to terpolymers, in which the weight ratio between (meth)acrylic acid or (meth)acrylate and maleic acid or maleate varies between 1:1 and 4:1 and preferably between 2:1 and 3:1 and particularly preferred between 2:1 and 2.5:1. In that respect, quantity as well as weight ratios relate to the acids. The second acid monomer or its salt may also consist of a derivative of an alkyl sulfonic acid that in the second position is substituted with an

alkyl rest and preferably with a C₁₋₄-alkyl rest or an aromatic rest that is preferably obtained from benzene or benzene derivatives.

In that regard, preferred terpolymers contain between approximately 40 and 60% by weight and preferably between 45 and 55% by weight (meth)acrylic acid or (meth)acrylate and particularly preferred acrylic acid or acrylate, between approximately 10 and 30% by weight and preferably between approximately 15 and 25% by weight methallyl sulfonic acid and as third monomer between approximately 15 and 40% by weight and preferably between approximately 20 and 40% by weight of a carbon hydrate. In that regard, this carbon hydrate may consist of a mono-, di-, oligo-, polysaccharide, in which case mono-, di- or oligosaccharides are preferred and saccharose is particularly preferred. The utilization of this third monomer leads to the introduction of predetermined breaking points in the polymers that are responsible for the biological polymer degradability. The utilized terpolymers can be prepared with known and common methods. Preference is also given to the use of terpolymers that are completely or at least partly neutralized, particularly to more than 50% in relation to the existing carboxyl groups.

Polyacetal carbonic acids like those obtained with a polymerization of esters from the glycol acid, introduction of stable terminal end groups and saponification to form sodium and potassium salts can also be used. Also appropriate are polymeric acids like those obtained with a polymerization of acrolein and a disproportioning of the polymers according to Canizarro with strong alkalis. They are basically build-up from acrylic acid units and vinyl alcohol units or acrolein units.

The percentage content of organic builders that contain carboxyl groups in the agent in accordance with the invention can reach approximately 10% by weight and preferably vary between approximately 1% by weight and 7.5% by weight and particularly preferred between approximately 2% by weight and 5% by weight and that of polyphosphonic acid can reach approximately 3% by weight and preferably varies between approximately 0.05% by weight and 1.5% by weight and particularly preferred between approximately 0.1% by weight and 1% by weight.

Other usable builders consist of crystalline alkali silicates as well as fine-particle alkali alumosilicates and particularly zeolites of the type NaA. Suitable zeolites exhibit a calcium-bonding power that ranges between 100 and 200 mg CaO/g (according to the data given in DE-C 24 12 837). Their particle size generally varies between 1 μ m and 10 μ m. They are used in the dry state. The water contained in the zeolites in the bonded form has no disturbing effect in this case. As crystalline silicates that may be present alone or in a mixture with the above-mentioned alumo- silicates, one preferably uses crystalline layer silicates of the formula NaMSi_x·O_{2x+1}·yH₂O, where M represents sodium, x a number between 1.9 and 4 and y a number between 0 and 20; 2,3 or 4 are preferred numbers for x. Such crystalline layer silicates are described in EP-A 0 164 514, for example. Particularly preferred are the β - as well as the ä-sodium disilicate Na₂Si₂O₅·yH₂O, in which case β -sodium disilicate may be produced with the method described in WO-A 91/08171. Suitable crystalline silicate is commercially available under the names SKS-6 (manufactured by Hoechst) and Nabion 15 (manufactured by Rhöne-Poulenc). The content of inorganic structure substances in the cleaning agent or in HGSM used by hand may reach up to approximately 35% by weight, preferably up to approximately 25% by weight and varies in a particularly preferred

manner between approximately 10% by weight and 25% by weight.

It is preferred that the cleaning agent in accordance with the invention and particularly HGSM contain no phosphate. When a phosphate content does not raise any ecological concerns (such as in the case of a sewage water treatment that removes phosphate), polymeric alkali phosphates such as sodium tripolyphosphate can also be present. Their percentage content may reach up to approximately 20% by weight in relation to the whole agent, in which case the percentage content of the other solid substances such as alkali silicate and/or alumo-silicate is reduced accordingly. The percentage content of tripolyphosphate preferably does not exceed 10% by weight.

The listed builders can be used in the agent in accordance with the invention individually or as a mixture of two or more of them. The total content in the agent in accordance with the invention of a builder or a mixture of two or more builders may reach up to approximately 5% by weight and preferably varies between approximately 0.1% by weight and 3% by weight and in a particularly preferred manner between approximately 0.5% by weight and 1.5% by weight.

The cleaning agent in accordance with the invention may contain an abrasive or a mixture of several abrasives to a content of approximately 70% by weight. The abrasive preferably consists of fine particles with an average grain size of between approximately 5 μ m and 100 μ m, in which case not more than 10% of the particles may be larger than 150 μ m. In a preferred manner, the average grain size of the particles that form the solid phase varies between 10 μ m and 80 μ m and particularly between 10 μ m and 60 μ m, in which case the maximum grain size is less than 200 μ m and particularly less than 150 μ m. The average grain size refers to the volume distribution of the particles that is determined with known methods (such as a Courier counter).

The abrasive may consist of a substance that is or is not soluble in water. Abrasives that are not soluble in water and can be used within the scope of this invention consist of quartz powder, marble powder, chalk, pumice stone, layer silicate and/or feldspar.

Water-soluble abrasives generally consist of water-soluble salts selected from the group of chlorides, carbonates, hydrogen carbonates, sulfates, phosphates, borates or silicates. They preferably consist of alkali metal salts and particularly preferred of the salts of sodium and/or potassium.

Water-soluble abrasives are preferably used for so-called "two-in-one" products that can be used in the concentrated as well as diluted form. Although the use of water-soluble abrasives in water-containing agents is possible when the quantity of the added abrasive exceeds the dissolving power of the water in relation to the abrasive substance, such a use is not preferred.

Abrasives may be present in the agent in accordance with the invention individually or as a mixture of two or more abrasives at a percentage content of up to approximately 70% by weight and the content preferably varies between approximately 30% by weight and 65% by weight and particularly preferred between approximately 40% by weight and 60% by weight.

Dyes and aromatics may be present in the agent in accordance with the invention at a low

total quantity of up to approximately 3% by weight.

The cleaning agent in accordance with the invention may be formulated in a solid form, as a paste or as a liquid and contains the tenside mixture in accordance with the invention at a quantity of up to approximately 99% by weight. In a preferred manner, the agent in accordance with the invention contains the tenside mixture in accordance with the invention at a quantity of between approximately 3% by weight and 50% by weight and particularly preferred at a quantity of between approximately 5% by weight and 30% by weight.

Formulation examples for cleaning agents in accordance with the invention contain approximately

- 9% by weight Gemini tenside (dimer diolether sulfate sodium salt, 20 EO)
- 6% by weight APG 600[®] (Henkel, Düsseldorf)
- 3% by weight cocinic amido propyl betaine
- 6% by weight C₁₂₋₁₄-fatty alcohol sulfate sodium salt.

or

- 13% by weight Gemini tenside (dimer diolether sulfate sodium salt, 20 EO)
- 5% by weight APG 600[®] (Henkel, Düsseldorf) 2% by weight APG 220[®] (Henkel, Düsseldorf)
- 4% by weight cocinic amido propyl betaine
- 8% by weight C₁₂₋₁₄-fatty alcohol sulfate sodium salt
- 1.5% by weight Carbopol 880[®] (B.F. Goodrich, OH, USA)

or

- 4% by weight Gemini tenside (dimer diolether sulfate sodium salt, 20 EO)
- 3% by weight Dehydol 980® (Henkel, Düsseldorf)
- 1.5% by weight C₁₂₋₁₄-fatty alcohol sulfate sodium salt.
- 0.5% by weight sodium gluconate
- 1% by weight C_{12-14} -fatty acid sodium salt,

in which case the part required to reach 100% consists of further additives and/or solvents, preferably of water, as indicated within the scope of this text.

The object of the invention also consists in the use of a tenside mixture that contains

between 0.1% by weight and 99% by weight of at least one tenside with at least two a) hydrophilic and at least two hydrophobic groups, in which case the hydrophilic groups and the hydrophobic groups are separated by a linear or cyclic spacer (Gemini tenside) that contains at least four C-atoms, as component A,

and

b) between 0 and 99% by weight of at least one non-ionic tenside that is not a Gemini

tenside as component B

and/or

c) between 0 and 99% by weight of at least one anionic tenside that is not a Gemini tenside as component C, in which case the sum of the percentage contents of components A, B and C must be 100%, in a cleaning agent and particularly in HGSM.

The following examples shall explain the invention in more detail; however, they have no restricting effect.

Examples:

The following compounds were used as components A, B and C:

Component A: Dimer diolether sulfate sodium salt (20 EO)

Component B: C₁₂₋₁₄-alkyl polyglycoside with an oligomerization degree of approximately 1.5

Component C: C₁₂₋₁₄-alkyl sulfate sodium salt

The lab standard consisted of a tenside mixture containing

- 60% by weight alkyl benzene sulfonate sodium salt
- 40% by weight C₁₂₋₁₄-fatty alcohol sulfate-2EO-sodium salt

as an aqueous solution with a total of 10% by weight active substance.

Example 1:

40% by weight of component A and 60% by weight of a 50% by weight aqueous solution of component B were stirred to form initial mixture V. This initial mixture V was then mixed with component C at the mixing ratios shown in Table 1 and was diluted with water to an active substance content of 10% by weight.

Of the thus obtained mixtures in accordance with the invention, 0.4 g (AVO-Soiling) or 0.5 g (Rita-Soiling) were added to approximately 10 liter water at a temperature of approximately 40 °C (AVO-Soiling) or approximately 45 °C (Rita-Soiling). Saucers that were previously soiled in a corresponding manner were then cleaned in this liquid until the foam cover covered only 50% of the cleaning liquid.

For comparison, identical quantities of the lab standard were added to 10 liter water at temperatures of 40 $^{\circ}$ C or 45 $^{\circ}$ C - identical to the above tests - and the flushing process was repeated. The results are shown in Table 1.

Table 1

Mixing ratio	Flushing results (%
	of the lab standard)

V	С	Rita	AVO
100	0	77	97
80	20	108	127
60	40	115	121
40	60	87	118
20	80	62	97
0	100	38	36
Dita - Boof dring	sing Cailing		

Rita = Beef dripping Soiling

AVO = Soiling based on lard and olive oil

Example 2:

20% by weight of component A and 80% by weight of a 50% by weight aqueous solution of component B were stirred to form initial mixture V. This initial mixture V was then mixed with component C at the mixing ratios shown in Table 1 and was diluted with water to an active substance content of 10% by weight. Of the thus obtained mixtures in accordance with the invention, 0.4 g (AVO-Soiling) or 0.5 g (Rita-Soiling) were added to approximately 10 liter water at a temperature of approximately 40 °C (AVO-Soiling) or of approximately 45 °C (Rita-Soiling). Saucers that were previously soiled in a corresponding manner were then cleaned in this liquid until the foam cover covered only 50% of the cleaning liquid.

This was again compared with the lab standard and the results are summarized in Table 2.

Table 2

Mixing ratio		Flushing results (% of the lab standard)		
V	C	Rita	AVO	
100	0	100	142	
80	20	123	155	
60	40	123	152	
40	60	92	133	
20	80	69	106	
0	100	38	39	

Rita = Beef dripping Soiling

AVO = Soiling based on lard and olive oil

Patent claims

1. A compound of the general formula I

/formula/ (I)

where R^1 and R^2 represent hydrogen and/or $C_{1\text{-}6}$ -alkyl independently of each other, R^3 , R^4 , R^5 and R^6 represent hydrogen or linear or branched alkyl rests with 4 to 24 C-atoms independently of each other, n represents numbers between 2 and 10, m and p represent numbers of 1 to 40 independently of each other, X and Y represent hydrogen, CH_2 -COOM or SO_3M independently of each other and M represents hydrogen or alkali or earth alkali metal ion or quaternized nitrogen bases, in which

case one of the two rests of the rest pairs R³ and R⁴ as well as R⁵ and R⁶ must represent hydrogen.

2. A tenside mixture that contains

a) between 0.1% by weight and 99% by weight of at least one tenside with at least two hydrophilic and at least two hydrophobic groups, in which case the hydrophilic groups and the hydrophobic groups are separated by a linear or cyclic spacer (Gemini tenside) that contains at least four C-atoms, as component A,

and

b) between 0 and 99% by weight of at least one non-ionic tenside that is not a Gemini tenside as component B,

and/or

- c) between 0 and 99% by weight of at least one anionic tenside that is not a Gemini tenside as component C, in which case the sum of the percentage contents of components A, B and C must be 100%.
- 3. A tenside mixture in accordance with claim 1, characterized by the fact that its component A contains at least one dimer alcohol-bis-ether sulfate and/or trimer alcohol-tris-ether sulfate that can be produced by reacting the addition reaction products of dimer- and/or trimer alcohols and alkylene oxides or a mixture of such addition reaction products with a sulfating agent and by then neutralizing this with an aqueous base.
- 4. A tenside mixture in accordance with claim 2, characterized by the fact that its component A has at least one compound of the general formula I

where R^1 and R^2 represent hydrogen and/or $C_{1\text{-}6}$ -alkyl independently of each other, R^3 , R^4 , R^5 and R^6 represent hydrogen or linear or branched alkyl rests with 4 to 24 C-atoms independently of each other, m and p represent numbers of 1 to 40 independently of each other, X and Y represent hydrogen, $CH_2\text{-}COOM$ or SO_3M independently of each other and M represents hydrogen or alkali or earth alkali metal ion or quaternized nitrogen bases, in which case one of the two rests of the rest pairs R^3 and R^4 as well as R^5 and R^6 must represent hydrogen.

5. A tenside mixture in accordance with claim 4, characterized by the fact that R¹ and R² represent hydrogen, R³ and R⁴ represent an unbranched alkyl rest with more than 10 carbon atoms, in which case the respective remaining rest represents hydrogen, R⁵ and R⁶ represents an unbranched rest with more than 10 carbon atoms, in which case the respective remaining rest must represent hydrogen and X and Y represent SO₃Na.

6. A tenside mixture in accordance with claims 2 through 5, characterized by the fact that it contains at least one compound of the general formula II as component B

/formula/ (II)

where R^3 represents a linear or branched C_{6-22} -alkyl rest, Z represents any mono- or oligosaccharide building block and x represents a number of between 1 and 5.

- 7. A tenside mixture in accordance with claims 2 through 6, characterized by the fact that it has at least one anionic tenside selected from the group of alkyl sulfates, alkyl ether sulfates, alkane sulfonates, alkyl benzene sulfonates or olefin sulfonates, as component C.
- 8. A tenside mixture in accordance with claims 2 through 7, characterized by the fact that it has at least one alkyl sulfate as component C.
- 9. A tenside mixture in accordance with one of claims 2 through 8, characterized by the fact that it contains
 - between 0.1 and 99% by weight component A,
 - between 0 and 99% by weight component B and
 - between 0 and 99% by weight component C.
- 10. Use of a tenside mixture that contains
 - a) between 0.1% by weight and 99% by weight of at least one tenside with at least two hydrophilic and at least two hydrophobic groups, in which case the hydrophilic groups and the hydrophobic groups are separated by a linear or cyclic spacer (Gemini tenside) that contains at least four C-atoms, as component A,

and

b) between 0 and 99% by weight of at least one non-ionic tenside that is not a Gemini tenside as component B,

and/or

- c) between 0 and 99% by weight of at least one anionic tenside that is not a Gemini tenside as component C, in which case the sum of the percentage contents of components A, B and C must be 100%, in cleaning agents and particularly in HGSM.
- 11. Cleaning agents and particularly HGSM containing a tenside mixture that contains
 - a) between 0.1% by weight and 99% by weight of at least one tenside with at least two hydrophilic and at least two hydrophobic groups, in which case the hydrophilic groups and the hydrophobic groups are separated by a linear or cyclic spacer (Gemini tenside) that contains at least four C-atoms, as component A,

and

b) between 0 and 99% by weight of at least one non-ionic tenside that is not a Gemini tenside as component B,

and

- c) between 0 and 99% by weight of at least one anionic tenside that is not a Gemini tenside as component C, in which case the sum of the percentage contents of components A, B and C must be 100%.
- 12. Cleaning agents and particularly HGSM in accordance with claim 11, characterized by the fact that the tenside mixture is present at a quantity of between 3% by weight and 50% by weight.
- 13. The use of compounds of the general formula I

/formula/ (I),

- where R^1 and R^2 represent hydrogen and/or $C_{1\text{-}6\text{-}}$ alkyl independently of each other, R^3 , R^4 , R^5 and R^6 represent hydrogen or linear or branched alkyl rests with 4 to 24 C-atoms independently of each other, n represents numbers of between 2 and 10, m and p represent numbers of between 1 and 40 independently of each other, X and Y represent hydrogen, CH₂-COOM or SO₃M independently of each other and M represents hydrogen or alkali or earth alkali metal ion, in which case one of the two rests of the rest pairs R^3 and R^4 as well as R^5 and R^6 must represent hydrogen - in laundry detergents, cleaning agents for hard surfaces, body cleansing agents, cosmetics, dish washer detergents, dish detergents, as industrial emulsifiers, wetting agents, dispersing agents, particularly in lacquers and paints, demulsifiers, hydrotropic agents, antistatic agents, additives for the oil industry, fuel additives or for uses in the metal and textile process industry.